X-RAY FLUORESCENCE SPECTROMETRY IN GEOLOGICAL SAMPLES

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ABSTRACT

Geological samples comprising of various rocks, ores and minerals need to be studied for their elemental chemical data. X-ray fluorescence spectrometry is a precise and accurate analytical technique for determining elements from atomic No.4 (boron) to 92 (uranium) at concentration levels of 100% to a few parts per million (ppm) in solids, liquids and powders. The non-destructive nature of analysis, speed, versatility, automation, sensitivity, selectivity, large sample throughput have made XRF technique a widely practised and well established technique for the determination of major, minor and trace elements in rock samples.

INTRODUCTION

X-rays are electromagnetic radiations having a wavelength range of 10^{-5} A° to 100 A°. Spectral region of interest in practical XRF spectrometry is 0.1 A° to 20A°.

Origin of spectra :

(a) Orbital electrons are expelled from inner (K, L, M .....) shells of the atom.

(b) Electrons from outer shells fall into the vacancies.

(c) Difference in energy is emitted as an X-ray photon.

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XRF SPECTROMETRY IS IN GENERAL OF TWO TYPES :

Wavelength dispersive XRF spectrometry (WDXRF) : X-ray spectral lines of all elements in the sample are excited. Simultaneously, then separated on the basis of their wavelengths prior to detection.

Energy dispersive XRF spectrometry (EDXRF) : X-ray spectral lines of all elements in the sample are either excited separately or are excited simultaneously, then separated by means other than walvelength or energy dispersion.

WDXRF SPECTROMETRY

Principle : XRF spectrometry is a group of non-destructive instrumental method of qualitative and quantitative analysis of chemical elements based on measurement of the wavelengths and intensities of their X-ray spectral lines emitted by secondary excitation.

i) The X-ray tube produces the primary X-ray beam

ii) The primary X-ray beam irradiates the rock sample and excites each chemical element to emit its characteristic X-ray spectrum.
   a) The wavelength of each spectral line is characteristic of the element present.
   b) The intensity of each line is directly related to the concentration of the element present in the sample.

iii) The collimator makes the secondary X-rays parallel.
The crystal acts as a monochromator.

iv) The diffracting crystal specially disperses the secondary X-rays causing each analyte line to go in a different direction.

v) The detector receives each wavelength diffracted by the crystal and for each X-ray photon produces an output pulse of electric current having amplitude proportional to the incident X-ray photon energy.

vi) The preamplifier and amplifier amplify these electric pulses linearly.

Qualitative Analysis

a) The goniometer (collimator-crystal-detector system) is scanned over its full practical range (20-140° 2θ).
b) The recorder chart records peaks on a grid of intensity vs 2θ (λ).
c) The elements present are detected from the peak positions (2θ, λ).
d) From the peak heights (intensity), the elemental concentration (semi quantitative) can be estimated.

Quantitative Analysis

a) The goniometer is set at fixed 2 θ (λ) from a specified element or analyte line e.g. Fe Kα.
b) Fe Kα intensity is measured from each sample and from a series of standards in which Fe concentration is known.
c) A calibration curve, Fe Kα vs Fe concentration is prepared from the standard data.
d) Fe Kα intensity from each unknown sample is applied to the curve to calculate Fe concentration.
e) This sequence is followed for all the chemical elements to be determined.

Specimen preparation

Any treatment other than simply cutting to appropriate size, to which the sample is subjected prior to its presentation to the spectrometer :

a) Chemical
b) Physical
c) Both

Specimen forms :

1) Solids
2) Powders
3) Briquettes
4) Fusion Products
5) Liquids, solution
6) Supported specimen
   (a) Filter paper
   (b) Mylar film

Need for preparation

1) Not required for qualitative analysis.
2) X-ray spectrometer can accommodate the sample in may forms.
3) XRF can analyse the samples in their as-received from faster than any other method available.

WHY TO PREPARE OR CHANGE THE FORM

I a) Rock sample is a heterogeneous mixture of different minerals present and it is necessary to make the sample homogeneous.
   b) Surface layer may not be representative of the bulk specimen.
   c) Particle size distribution may vary from sample to sample.
   d) Porosity varies from specimen to specimen.

II ***Additions***

a) Internal standard
b) Dilution method
c) Standard addition

III. Chemical separation may be required for determining some of the trace elements or rare earth elements.

IV Available standards must be matched. Standards are not available in the as-received form of the sample.

ADVANTAGES OF XRF SPECTROMETRY

1. Simplicity of x-ray spectra
   (a) Relatively a few lines
   (b) Each element has its own line having relationship between λ and Z.
   c) Independent of chemical state as dealing with inner most electrons of the atomic orbit.

2. Method applicable to a very wide range of specimen form.
3. Non-destructive method of chemical analysis.
4. Applicable to a very wide range of chemical concentration i.e. ppm to 100%.
5. High precision and accuracy.
6. Selectivity and sensitivity.
7. Rapid and convenient.
8. Cost affective.
9. Very little sample preparation is required.

LIMITATIONS

1. Only a thin surface layer contributes the measured analyte line intensity
2. Subject to particle size, surface texture and matrix effect (absorption-enhancement effects)
3. Standards must be similar to the samples in physical form, matrix composition, concentration range and particle size.

SOURCES OF ERROR IN XRF ANALYSIS

1. ***Statistical counting error:*** Arise due to randon time distribution of x-ray photons.

2. ***Instrumental error :*** Arises due to short term and long term instrumental drift, fluctuation and instability in instrumental components, conditions and parameters :
   (a) x-ray tube kV and mA
   (b) Intensity of the primary x-ray beam
   (c) Due to change in temperature, d spacing of the crystal may change.
   (d) Gas amplification of gas flow counter due to changes in pressure, temperature and detector potential.
   (e) Pulse height distribution shift and distortion.

3. ***Operational Error :*** Caused by the slight non-reproductibility in instrumental settings like
   (a) x-ray tube kV mA
   (b) 2θ
   (c) Amplifier gain
   (d) Detector potential
   (e) Pulse height selection window

4. ***Specimen error***
   (a) Absorption-enhancement effect
   (b) Position effect including insertion error
      (1) Specimen plane
      (2) Takeoff angle
      (3) Position
      (4) Orientation
      (5) Flatness

(c) Physical form

(1) Thickness (if less than infinitely thick)

(2) Heterogeneity of composition (very severe ingeological samples)

(3) Hetrogeneity of density

(4) Surface texture

(5) Particle size

5. Spectral line interference.

XRF SPECTROMETRY - COMPONENTS

A. X-ray tube

1. Function : To generate the primary x-ray beam that excites the analytical x-ray spectrum.

2. Anode targets available

Cr, Sc ---------- Light elements

Mo, Ag ----------Medium elements - Rb, Sr

W ---------- Fe, Ni

Pt, Au ---------- Heavy elements

Rh ---------- Multipurpose

DUAL ANODE (sc-Mo) ---- Low kV gives Sc spectra while high kV gives Mo spectra

B. X-ray tube power supply : Intensity is directly related to power supply.

1. Function : To supply to the cathode filament and power to the x-ray tube.
2. Maximum kV out put : Varies with different XRF from 60, 75 to a maximum 100 kV.

C. Specimen chamber

D. Spectro goniometer

1) Collimator

a) *Function :* Blocks divergent x-rays and provides parallel secondary x-ray beam

b) *Structure* - Spaced parallel metal foils

1) Length (2.5 - 10 cm)

2) Spacing (0.1 - 1.0 mm)

c) *Position*

1) Source collimator (primary) between specimen and crystal.

2) Detector collimator (secondary) between crystal and detector

Coarse (550 μm) B to Ca

Fine (150 μm) Ti to U

A fine collimator gives better resolution i.e. separation of close lines but results in lower intensity.

2) Crystal

a) Function - Specially disperses the polychromatic x-ray beam from the specimen, causing each spectral line to go in a different direction - acts as a monochromator

b) Many crystals are required for different wavelength regions. The longest wavelength a crystal can diffract is 2 d A° which is twice its own interplannar spacing.

The different crystals commercially available are (2d, increase)

LiF 420	2.0 A°
LiF 220	2.85 A°
LiF 200	4.0 A°
Ge	6.53 A°
PET	8.73A°
T1AP	25.75A°

PX-1 to PX-4 (Smaller 2d value crystal results better resolution)

3. ***Radiation path*** :

a) Air < 2.5 A° (Ti Kα) z = 9 to 21

b) Vacuum > 6 A° (PKα) z = 21 to 92

c) Helium - liquid samples - light elements

E. DETECTOR

1. ***Function*** : Coverts each incident absorbed x-ray photon into a pulse of electric current having amplitude proportional to the incident photon energy.

2. ***Type***

a) Proportional (gas filled-sealed or flow) for determining Bto Se (z = 34).

b) Scintillation Z = 50 to 90
Both (F&S) are used to determine z=34 to 50.

c) Solid state semi conductor, lithium drifted Si.

F. READOUT AND DISPLAY

1. Preamplifier - amplifies detector output pulses linearly
2. Amplifier - further amplifies pulses linearly
3. Pulse height selector - Passes all pulses having amplitude greater than the baseline potential through the set 'window'
4. Ratemeter
5. Recorder
6. Scaler - Counts the pulses
7. Timer - times the duration
8. Printer - print out the accumulated counts from the scaler.

Fully automatic XRF spectrometers are of two kinds :

1. ***Sequential :*** A single collimator - crystal - detector system is programmed to index automatically in sequence to the setting for each

analyte line and its background and accumulate counts for each. It is very useful in R&D laboratories where one needs to determine a very wide range of elements.

2. Simultaneous : upto 22 channels (i.e. collimator - crystal - detector) are arranged around the specimen each with its own readout system and each channel set for a different analyte line. This kind of system is good where only some limited fixed number of elements are to be analyzed e.g. cement and steel industries.

APPLICATION IN GEOLOGY

X-ray fluorescence spectrometry is one of the most powerful analytical tool in the study of geological samples. No modern geological institute can function without the presence of XRF spectrometer. It is the fastest and non-destructive analytical tool to study the different types of geological samples having different concentration range of various elements present. The different rock types can be divided in four types on the basis of silica content.

1. Acidic - SiO_2 66% to 90%
2. Intermediate - SiO_2 55% to 66%
3. Basic - SiO_2 45% to 55%
4. Ultrabasic - SiO_2 less than 45%

All other elements present in the rock samples vary depending on the variation of silica concentration. XRF technique has been applied successfully to a number of geological problems requiring rapid answers such as the identification of unknown rock types, minerals, ores, geochemical prospecting etc.

Sample preparation : All the rocks are heterogeneous mixture of different minerals present and therefore, it is necessary to have some sample preparation technique to remove the effect of heterogeneity.

First of all the rock sample is finely powdered to -300 mesh size and then either the fused glass beads (for determining major oxides) or pressed pellets (for determining trace elements) are prepared.

Line Overlapping : The major problem in performing XRF analysis is that of resolving overlapping lines. These interfering lines may be of the elements which are very close in wavelength and cannot be resolved because of the instrumental limitations or the lines diffracted in higher orders. If the interference is due to the first order lines, it can be removed by separating the lines by changing the collimator or crystal used in the analysis. First order lines can easily be resolved by selecting another crystal of smaller 2 d spacings. Other methods of resolving lines involve pulse-height discrimination, crystals which do not diffract in certain higher orders etc.

MATRIX EFFECT

The problem of matrix effect (enhancement or absorption) is very severe in XRF analysis of rock samples. The intensity of the analyte may be increased or decreased due to the presence of different elements present in the sample and will lead to the wrong results. There are different methods for dealing with matrix correction e.g.

1. Reference Rock Standards
2. Addition Method
3. Heavy absorber
4. Dilution
5. Internal Standard

1. Reference Stock Standard : The standards used in making calibration curves of intensities vs concentration of the analyte must be of similar matrix with reference to the elements present and their

chemical composition. It is not possible to use a curve prepared for acidic rock sample to calculate the elements in basic or ultrabasic concentration range. Such a procedure gives rise to a family of analytical curves required e.g. basalt standards for basalt samples and granite standards for granite samples. It is however, often difficult to find such similar standards. If the materials are too variable in composition, they can no longer be safely considered as of the same type. Other possibilities to remove or to reduce matrix effects are to prepare natural, hemi and synthetic standards of the similar composition or to use preanalysed samples of the same rock type by using some classical method of analysis as standard or reference samples to prepare calibration curves.

2. ***Addition Method :*** In the absence of suitable similar standards, the method of addition is useful for performing an occasional analysis. One has to make a rough estimate of the concentration of the element sought. Then a small but known amount of the element is added to an aliquot of the unknown. By measuring the intensities of unknown and then the unknown plus the addition, it is possible to solve for the original composition. This method assumes a linear relationship between composition and intensity. It is extremely important to make homogeneous dispersion of the element added and one should take great care to grind and mix the powder thoroughly.

3. ***Heavy absorber :*** Different types of heavy absorbers are used in making fused glass beads using lithium tetra/meta borate and rock samples. A heavy element such as lanthanum oxide is added in the fused bead before melting to serve as an absorption buffer. In principle, a high atomic number element is added in an amount such that the variation in concentration of absorbing elements in the sample will not materially effect the overall absorption of the prepared fused bead for the element to be determined. The most commonly used

absorber is lanthanum due to its high absorption coefficient and its availability as the oxide at a reasonable cost. Recently it was found that lanthanum lines interfere with the sodium lines and it may not be possible to determine the sodium concentration in rock samples by using lanthanum absorber. The author has made some studies and it was observed that it is better to use samarium in place of lanthanum if one wishes to determine sodium also in the rock samples.

4. Dilution : The adverse effect of different elements in a matrix on each other can be minimized upto some extent by large dilution. A dilution of 100:1 has shown accuracies comparable to the internal standard method but in a much simpler way. The major disavantage of dilution technique is the loss of sensitivity and detection limits specially for the elements present in lower concentration range.

5. Internal Standard : One of the simplest and most effective means of dealing with matrix effect problem in rock analysis is the internal standard method. One needs an element either present in the rock sample or added to the various samples and standards in constant amount, which will be enhanced or absorbed to the same extent as the element being determined. This can easily be done if the sample is finely powdered or if fusion technique is used. The internal standard element should be as close as possible in atomic number. If the atomic number of the element is Z then the internal standard element can be Z + 1. For the light elements (Ti and lighter) Z-1 elements will strongly absorb Z elements and therefore, Z + 1 elements are a better choice. It is extremely important to distribute and mix the internal standard element homogeneously through the sample which requires very small particle size and extensive grinding.

DATA COMPUTATION

The spectrometer measures the X-ray photons and displays as intensity data. This needs to be converted into elemental concentration by using different mathematical models.

The concentration C of an element can be calculated from C = D + E R where R is the net intensity after subtracting background, D is the intercept and E is the slope of the calibration curve after doing the regression analysis. This linear equation assumes that there are no or negligible matrix effects which is possible only in cases where elemental concentrations are reasonably equal between samples and standards. Different calculation models are used in computing the concentration data. Some of them are :

1. Lucas-Tooth Pyne Model : This model is suitable for the analysis of samples with small elemental concentration ranges. The correction is based on the intensity of the interfering element and the advantage is that the correction factors can also be derived for those elements for which the concentration is not known.
The correction formula is :

$$C_i = (D_i + E_i R_i)\ (1 + \Sigma_j \alpha_{ij}\ R_j/100)$$

2. De Jongh Model : This model is based on the concentrations of the different elements present and uses a set of simulataneous equations. In this model fundamental influence coefficient (alphas) can be applied. The correction formula is :

$$C_i = (D_i + E_i R_i)\ (1 + \Sigma_j \alpha_{ij}\ C_j/100)$$

This method is most extensively used and has proved successful for geological samples.

The alphas are constant for a given type of rock samples, X-ray tube and spectrometer settings. The application of theoretical alphas is extremely useful if only a small number of standards are available and can not be calculated from regression curves.

3. Rasberry - Heinrich Model : This model covers an extra wide range of concentration of different elements. The formula is :

$C_i = (D_i + E_i R_i) [1 + \Sigma_j \alpha_{ij} C_j/100 + \Sigma_k \beta_{ik} C_k/100 (1 + C_j/100)^{-1}]$

The second correction term provides a better fit. This takes help of calculation of beta correction factors alongwith alphas but need to be calculated on line.

Recently some new softwares have come in the market which can convert the intensity data into elemental concentration with the help of pure elemental standards or by using only one standard. The main problem faced in the analysis of geological samples is non-availability of suitable rock standards for doing regression analysis with full confidence. Now this problem is not so accute with the availability of "standard less software" though one has to use with caution as they are not yet proved as quantitative.